Climatic Drivers for Multi-Decadal Shifts in Solute Transport and Methane Production Zones within a Large Peat Basin

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Key Points

Methane production zones are finely tuned to climate-driven transport systems in a 7600 km^2 peat basin.

During dry decades, a weak recharge regime restricts CH_4 production to shallow peat depths

During wetter decades, deeper recharge extends CH_4 production to the entire peat profile

Abstract

Northern peatlands are an important source for greenhouse gases but their capacity to produce methane remains uncertain under changing climatic conditions. We therefore

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analyzed a 43-year time series of pore-water chemistry to determine if long-term shifts in precipitation altered the vertical transport of solutes within a large peat basin in northern Minnesota. These data suggest that rates of methane production can be finely tuned to multi-decadal shifts in precipitation that drive the vertical penetration of labile carbon substrates within the Glacial Lake Agassiz Peatlands.

Tritium and cation profiles demonstrate that only the upper meter of these peat deposits was flushed by downwardly moving recharge from 1965 through 1983 during a Transitional Dry-to-Moist Period. However, a shift to a moister climate after 1984 drove surface waters much deeper, largely flushing the pore waters of all bogs and fens to depths of 2 m. Labile carbon compounds were transported downward from the rhizosphere to the basal peat at this time producing a substantial enrichment of methane in $\Delta^{14}C$ with respect to the solid-phase peat from 1991 to 2008. These data indicate that labile carbon substrates can fuel deep production zones of methanogenesis that more than doubled in thickness across this large peat basin after 1984. Moreover, the entire peat profile apparently has the capacity to produce methane from labile carbon substrates depending on climate-driven modes of solute transport. Future changes in precipitation may therefore play a central role in determining the source strength of peatlands in the global methane cycle.

Index terms (0426) Biosphere/atmosphere interactions, (428) Carbon cycling, (0497) Wetlands, (1832) Groundwater transport, (1829) Groundwater hydrology

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Introduction

Boreal peatlands have counterbalancing roles in the global climate system functioning as both an important source for methane and sink for carbon dioxide [*Matthews,* 2000*; Frolking and Roulet,* 2007; *Kirschke et al.,* 2013]. The growth of this large carbon reservoir had a net cooling effect on global climates during the Holocene as 400-500 Pg of carbon were transferred from the atmosphere to this terrestrial sink [*Gorham,* 1991]. In contrast, the accumulation of this massive pool of organic carbon created a natural incubator for the production of methane, a potent greenhouse gas. Despite the importance of peatlands as sources for methane, considerable uncertainty remains regarding the dynamics of methane production within peat profiles and its relationship to climatic drivers. A central problem concerns the depth of methane production zones within peat deposits and their potential linkage to climatic drivers.

A broad consensus exists that organic matter accumulates in freshwater peatlands because a waterlogged peat profile maintains anoxic conditions that restrict the breakdown and mineralization of organic matter to the least efficient metabolic pathways of fermentation and methanogenesis [*Clymo,*1984]. However, two opposing views prevail with regard to the mobility of pore waters and reactivity of organic matter in deep peat deposits. One school of thought assumes that methane production is largely limited to the uppermost peat strata just below the water table where methanogenesis is favored by the abundance of labile carbon compounds but inhibited below by the accumulation of refractory organic matter [*Blodau,* 2002; *Beer et al.,* 2008]. According to this model the deeper strata represent a nearly closed system with regard to solute transport [sensu *Ingram,* 1982, 1983] and the mineralization of organic matter to CH_4 and CO_2 [sensu *Clymo,* 1984]. This concept assumes 1) the deeper carbon mass consists largely of recalcitrant (non-reactive) organic compounds, 2) the accumulation of metabolic byproducts inhibit rates of carbon mineralization, 3) increasing cation exchange capacity of the peat with depth inhibits microbial activity, 4) the small particle size of the peat matrix creates very low intrinsic permeability, and 5) the small peat pores are readily occluded by methane bubbles [*e.g. Ingram,* 1982; 1983*; Clymo* 1984; *Clymo and Pearce,* 1995; *Baird and Waldron,* 2003*; Thomas and Pearce,* 2004; *Belyea and Baird,* 2006; *Beer et al.,* 2008].

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The other school contends that even slow transport systems in the deeper peat strata (i.e. catotelm) will determine the pore-water chemistry and affect rates of methanogenesis [*Siegel and Glaser*, 1987*; Glaser et al.,* 1997*; Reeve et al.* 2000, *2001*]. In particular, radiocarbon analyses indicate that methanogenesis is fueled by labile carbon substrates that are transported downward from the near-surface rhizosphere through the interconnected pore space to depths of 3-to-4 meters in large peatlands [*Chanton et al.,* 1995, 2008*; Chasar et al.,* 2000a, 2000b*; Corbett et al., 2013*a, *2015*]. Vertical transport of solutes through these peat deposits may be favored by the prevalence of macropores, secondary porosity created by migrating gas bubbles, or climatically driven flow systems acting on a highly deformable peat fabric.

In order to assess these opposing hypotheses we analyzed a 43-year dataset from the Glacial Lake Agassiz peatlands (GLAP) in northern Minnesota (Figure 1). This study area offers an unusual set of opportunities to track solute transport within a large peat basin and determine if climatic shifts can alter the vertical distribution of methane production zones. The GLAP comprises a large expanse of bogs and fens that have spread across a steep climatic gradient in northwestern Minnesota. In this hydrogeologic setting, three different tracers can be used to track solute transport systems through time. Calcium provides a conservative tracer for groundwater upwelling from the calcareous glacial deposits that underlie the peatlands, whereas tritium (^{3}H) can be analyzed to track the downward penetration of recharge from precipitation since the onset of nuclear weapons testing in the atmosphere. Radiocarbon (^{14}C) provides an additional tracer for tracking the downward transport of labile DOC (dissolved organic carbon) from its source in near-surface strata to its uptake by methanogens.

We therefore analyzed a 43-year record of the pore-water chemistry within the GLAP to determine whether shifts in solute transport could be related to long-term changes in regional precipitation. The main rationale for this study was to test the hypothesis that long-term shifts in precipitation patterns altered the depth of recharge and downward transport of labile dissolved organic matter through the peat profile. The scope of the chemical and climatic datasets, which extend over a large peat basin in northwestern Minnesota for multiple decades should provide a long-term perspective on the linkages among, climate, solute transport, and the depth of methane production zones.

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2. Study Area

The Glacial Lake Agassiz peatlands comprise a 7600 km^2 expanse of patterned bogs and fens in northwestern Minnesota between 48º 3' and 48º 35' N lat. and 95º 3' to 95º 40' W long. (Figure 1) [*Glaser,* 1992a]. This study area lies entirely within the lacustrine plain of former Glacial Lake Agassiz, a broad lowland that extends across most of northwestern Minnesota [*Wright,* 1972]. The lacustrine plain is underlain by deep glacial deposits composed of calcareous till and lacustrine sediments that are saturated with circumneutral groundwater characterized by high concentrations of Ca and Mg [*Bidwell et al.,* 1970*; Helgesen et al.,* 1975]. The surficial deposits range in thickness from approximately 20 to 45 m [*Siegel,* 1981] and cover metamorphic bedrock.

Despite a relatively dry regional climate, the entire lowland is prone to waterlogging because its sparse river system is inadequate to remove precipitation in excess of evapotranspiration from this region of low topographic relief [*Glaser et al.,* 2006]. Peatlands began to spread across this lowland after a climatic shift to cooler and moister conditions about 5000 years ago [*Janssen,* 1968] and now cover approximately 56% of the 7600 km^2 GLAP study area [*Glaser,* 1992a*; Glaser et al.,* 2006]. Peat accumulation created an array of very large and highly patterned raised bogs, fen water tracks, and bog-fen complexes that can individually exceed 100 km^2 in area with peat depths ranging from 3 to 5 m [*Glaser,* 1992b, *Glaser et al. 1981; 1997*]. Raised bogs are either forested or dominated by sedges but consistently have a continuous mat of *Sphagnum.* The surface waters on bogs are distinguished by a low pH (<4.2) and low concentrations of cations (e.g. Ca <2 mg l^{-1}) similar to that in precipitation [*Glaser,* 1992*; Glaser et al.,* 1990, 1997]. Fens, in contrast, can also be either forested or dominated by sedges but are distinguished by the presence of fen-indicator species and surface waters with a higher pH (>4.2) and higher concentrations of Ca (>2 mg l^{-1}) and other cations that are indicative of groundwater-derived alkalinity [*Glaser et al*., 1981, 1990; *Glaser,* 1992a]. The GLAP also contains a small number of spring fens that are localized zones for persistent groundwater discharge. Spring fens have distinctive surface-water chemistry (pH >6.8; Ca concentrations > 20 mg l^{-1}) but cover less than 1% of the GLAP. The vegetation/landform patterns of the GLAP are very similar to those found across other large peat basins in the continental interior of North America [e.g. Sjörs, 1963; *Vitt et al.,* 1994*; Glaser et al*., 2004a; *Glaser et al*., 2004b].

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The development of such large peat landforms across northwestern Minnesota is unexpected given the relatively dry climate and recurring droughts. The average annual precipitation in northwestern Minnesota was only 558 mm from 1885 through 2012 and regional dry periods recurred on seasonal to multi-decadal time scales according to weather records compiled by the National Climatic Data Center [*www.ncdc.noaa.gov*].

3. Sampling Strategy and Objectives

We first analyzed a 115 year record of weather observations across northwestern Minnesota to distinguish long-term trends in precipitation. This record was compared to a 43-year time series of geochemical and isotopic analyses of pore-water profiles within the GLAP with a focus on three different tracers (tritium, Ca^{2++}, and $\Delta^{14}C$). In addition we used $\delta^{13}C$-DIC to infer relative rates of methanogensis throughout the peat profile. These analyses included both published and unpublished data with an emphasis on the later.

Field sampling across the 7600 km^2 study area is limited by the very large size of the peatlands and the sparse regional network of roads, The first study [*Gorham and Hofstetter,* 1971] was therefore restricted to sites accessible by all-terrain vehicles, whereas after 1977 helicopters provided comprehensive access to the complete range of bog and fen sites of the GLAP. The sampling strategy combined synoptic sampling of a representative array of bog and fen sites across the entire GLAP with detailed analyses of the Red Lake [*sensu Glaser et al*., 1981] and Lost River [*sensu Siegel and Glaser,* 1987] bog-fen complexes (Figure 1, sites a-e). Many of the same sites were re-sampled after 1981 to provide a direct standard of comparison.

4. Methods

4.1 Regional Precipitation Record 1895-2012

The National Climate Data Center has compiled a regional dataset for weather measurements across northwestern Minnesota from 1895 through the present. The mean annual precipitation (MAP) data for this region was first plotted with respect to the average value for the record from 1895 to 2012. A 5-year moving average was next calculated to detect any

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longer term trends in precipitation. Box plots were then used to characterize the statistical distribution of MAP within the three principal periods for precipitation from 1916 through 2008 that became apparent from the plot of the moving average.

4.2. Normalizing the Tritium Time Series

A 43-year time series for tritium profiles from the Red Lake II (RLII) bog was compiled by combining data collected by Gorham and Hofstetter [1971] immediately after the bomb peak in the 1960s with pore-water profiles collected from this same site and adjacent areas in 1997-1998 and 2007-2008. Since tritium (^{3}H) is an unstable radioactive isotope all values in this dataset were first transformed to a uniform standard of comparison. The analytical solution for first-order decay [*Faure*, 1977] was used to adjust all tritium concentrations to a common end point assuming radioactive decay for all values continued to 2008:

$$N = N_o e^{-\lambda t} \quad (1)$$

where N is the final tritium concentration in Tritium Units (TU), N_o is the initial value in TU, e is the base of natural logarithms, λ is the decay constant of tritium, based on a half life of 12.32 years [*Lucas and Unterweger*, 2000], and t is the time interval from the sampling period to 2008. This equation was also used to standardize tritium values from the Ottawa precipitation curve, which is the longest continuous record for the tritium content of precipitation near the GLAP. The latitude of Ottawa, Canada (45° 25' N) is close to that of the Red Lake II bog crest (48º 15' N), and should therefore provide a representative record for assessing the past tritium content of precipitation for the GLAP.

4.3. Pore-Water Profiles

Pore-water profiles were collected from a representative array of peatland types across the Glacial Lake Agassiz peatlands on a roughly decadal timescale from 1981 through 2008. The longest records were based on the initial sampling of the Red Lake II bog crest for tritium [*Gorham and Hofstetter*, 1971] and Lost River bog-fen complex for cations [*Siegel and Glaser*, 1987]. These same sites were re-sampled during synoptic surveys of peat landforms across the entire GLAP from 1990 through 2008 [*Romanowicz et al.*, 1993, 1995*; Siegel et*

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al. 1995*; Glaser et al.,* 1997*; Rivers,* 1999*; Dasgupta,* 2010*; Levy et al.,* 2014]. The synoptic surveys included transects across several large bog complexes that extended downslope from the forested bog crests to 1) non-forested bog drains 2) poor-fen *Sphagnum* lawns, and finally 3) internal rich-fen water tracks [*sensu Glaser et al.,* 1981]. At each site a peristaltic pump was used to extract pore waters from piezometers inserted into the peat at 0.5 or 1 m depth intervals following procedures described by Chason and Siegel [1984], Siegel and Glaser [1987], and Romanowicz et al. [1995]. All pore-water samples were analyzed for cations using a DCP (Direct Current Plasma) emission spectrometer at Syracuse University. In 1998 and 2008 pore waters were also analyzed for tritium using standard procedures at the Environmental Isotope Laboratory, University of Waterloo. The precision of the tritium analyses was ± 6 tritium units (TU) but several samples were enriched for tritium to obtain values with a precision of ± 0.5 TU. Details on quality assurance can be found at www.uweilab.ca.

4.4 Binary-Mixing Models for Pore-Water Chemistry

A binary-mixing model was used to assess the effect of mixing a) recharge from the bomb-peak era with pore waters dating from the pre-bomb era and also b) recharge consisting of dilute precipitation with groundwater containing high concentration of cations. This model is based on the equation provided by Faure [1977, 1998]:

$$X_M = X_A f + X_B(1-f) \qquad (2)$$

where X_M is concentration of species X in the final mixture, X_A and X_B are the concentrations of species X in components A and B respectively, expressed in units of mass, and the fraction f is the product of A divided by A plus B. Peak values for tritium fallout during the bomb period were assumed to be 1000 and 2000 TU (= 89 and 179 $TU_{cor2008}$ respectively) based on values reported by Stewart and Wyerman [1970], Michel [1989], Clark and Fritz [1997], and Ferronsky and Polyakov [2012]. The tritium content in pre-bomb groundwater was assumed to be 5 TU_{1944} (=0.0475 $TU_{cor2008}$) based on Kaufman and Libby [1954]. Equation (2) was also used to assess mixtures of groundwater from the mineral substratum, which typically has Ca concentrations in excess of 100 mg l^{-1} [*Helgesen et al.,* 1975] with recharge from precipitation, which typically has Ca concentrations <2 mg l^{-1} in northwestern Minnesota [*Munger and Eisenreich,* 1983; *Berner and Berner,* 2012].

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4.4 Biogeochemistry

The methods for determining the radiocarbon signatures of methane dissolved in the pore waters follows that of Chanton et al. [1995], Chasar et al. [2000a; 2002], and Corbett et al. [2013a]. Pore waters were collected from the same range of bogs and fens in 1991 to 2008 using piezometers and a persistaltic pump by adjusting the speed to maintain a continuous stream of bubble-free water. The dissolved methane extracted from these samples was first combusted to CO_2 and then further converted to graphite [*Vogel et al.,* 1987] for radiocarbon analysis at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility. All ^{14}C data were corrected for fractionation effects by measuring the sample $^{13}C/^{12}C$ ratio and normalizing the ^{14}C results to a common $\delta^{13}C$ of -25‰. The fraction of modern carbon in these methane samples was estimated as a first approximation by using a binary-mixing model (Eq. 2) with the radiocarbon activity of modern (i.e. recently-fixed) carbon as one end member and the radiocarbon signature of the solid-phase peat at the sampling depth as the other end member. The radiocarbon signature of the peat at each sampling depth was obtained by dating samples from peat cores recovered with a piston sampler equipped with a 10-cm diameter stainless steel barrel and a cutting edge [*Wright et al.,* 1984].

The pore waters were analyzed for $\delta^{13}C$-DIC by direct injection to a GC (gas chromatograph) combustion-interfaced with a Finnegan MAT Delta V isotope ratio mass spectrometer (IRMS). The field sampling and lab analyses follow the methodology described by Chasar et al. [2000a, 2000b] and Corbett et al. [2013b].

4.5 Mixing Models for Carbon Isotopes

Equation 2 was used to assess the effect of adding $\delta^{13}C$-DIC produced by methanogenesis to a $\delta^{13}C$-DIC pool derived solely from atmospheric CO_2 (-8‰), soil carbonate (-11‰), or respiration and fermentation reactions, which are non-fractionating (-27‰). We varied the end member representing $\delta^{13}C$-DIC produced by methanogenesis between +10‰, which is typical for the deeper portions of peat or soil profiles [*Chasar et al.* 2000a*; Kendall and Doctor,* 2005; *Steinmann et al*., 2008; *Corbett et al* 2013b] and +21‰ for landfill leachate [*Games and Hayes,* 1976, 1979; 1977*; Baedecker and Back, 1979; Walsh et al.,* 1993].

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Landfill leachates probably represent an upper limit for the isotopic enrichment of δ^{13}C-DIC by methanogenesis because landfills contain a much richer supply of labile organic matter. The mixing models should provide a first approximation for the effect of adding DIC produced by methanogenesis to an existing DIC pool with the understanding that the actual δ^{13}C-DIC pool in natural peatlands is probably more complex because of multiple mixing and isotopic enrichment effects. Equation 2 was also used to estimate the fraction of recently-fixed carbon substrates in pore-water methane. The end member for recently-fixed carbon was set by the value of atmospheric CO_2 at the time of sampling reported by Hua et al. [2013] and Druffel and Griffin [1995], whereas the Δ^{14}C value of the peat at each sampling depth was used as the other endmember.

5. Results.

5.1 Climatic Shifts Across Northwestern Minnesota (1895-2012)

The 117-year precipitation record for northwestern Minnesota was divided into three multi-decadal periods using box plots, ranges of Mean Annual Precipitation, and a 5-year moving average with respect to the long-term average of 558 mm yr^{-1} (Figure 2). These analyses identified a long initial Dry Period, which persisted from 1911 to 1940 followed by a secular trend toward a moister climate (Figures 2 and 3). The average precipitation during the initial Dry Period was only 529 mm yr^{-1}, whereas the 5-year moving average showed a progressive downward trend in precipitation from 1916 to 1936 when the long-term record reached its nadir of 330 mm yr^{-1}. Although annual precipitation began rising after 1936, annual precipitation still remained below the long-term average of 558 mm yr^{-1} until 1941.

The regional climate became moister after 1940 as the average precipitation rose slightly to 569 mm yr^{-1} for the Transitional Dry-to-Moist Period (1941-1986). This period was characterized by frequent shifts in precipitation between 29 moist years that were wetter than the long-term year average and 16 years that were drier. This transitional climatic period was followed by the Moist Period (1991-2012), which was the wettest period on record with an average precipitation of 617 mm yr^{-1}. The Moist Period was marked by 11 years with more than 660 mm yr^{-1}, and four years with precipitation exceeding 700 mm yr^{-1}. Seasonal and annual droughts continued but were less frequent and much less intense.

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5.2 Tritium as a Tracer for Recharge after 1953

The radioactive nuclide tritium provides an important tracer for the movement of precipitation through groundwater flow systems because of its short half-life (12.36 years) and pervasive occurrence in precipitation. Although the distinctive signal of recharge from the peak of the "bomb" period has now largely dissipated, tritium can still be used to divide groundwater into three different age classes on the basis of the Ottawa tritium record [*Clark and Fritz*, 1997], once all values are normalized for radioactive decay through 2008 (Figure 4). Pre-bomb (<1945) levels of tritium in groundwaters are generally assumed to be less than 0.05 $TU_{cor2008}$ based on an analysis of vintage wines [*Kaufman and Libby*, 1954]. In contrast, recharge from the peak of the bomb era (1954-1971) was characterized by 12 bomb pulses in which tritium fallout exceeded 40 $TU_{cor2008}$ (Figure 4). After 1971, tritium levels fell below 40 $TU_{cor2008}$ but remained significant, ranging from 6 to 20 $TU_{cor2008}$ throughout this post-bomb era (1972-2008).

5.3 Pore-Water Geochemistry: 1965-1983

Gorham and Hoftsetter [1971] reported the first tritium profiles from the Glacial Lake Agassiz peatlands from 1965 to 1969. These profiles showed a distinct bomb peak in the uppermost 100 cm of the RLII bog followed by a rapid decline in TU below a depth of 180 cm. Their most detailed tritium profile in 1969 contained a distinct bomb peak of 46 $TU_{cor2008}$ at a depth of only 18 cm (Figure 5). Tritium concentrations then decreased nearly 2-fold to 26 $TU_{cor2008}$ at 120 cm depth, followed by a much steeper decline to about 6 $TU_{cor2008}$ at 180 cm depth, 3.4 $TU_{cor2008}$ at 330-350 cm depth, and concentrations of 0.35 $TU_{cor2008}$ at depths deeper than 350 cm that approach but slightly exceed those of pre-bomb levels.

A similar zonation pattern was found in the pore waters of the Lost River peatland from 1981 to 1983 (Figure 5). Siegel and Glaser [*1987*] reported that dilute pore waters similar to that of precipitation were confined to the upper meter of the peat profile of the bog and fen water track sites at Lost River (sites d and e in Figure 1) from 1981 through 1983 [*Siegel and Glaser*, 1987]. Below 100 cm the pore waters were more characteristic of geogenous groundwater with Ca concentrations exceeding 75 mg l^{-1} and pH values exceeding 6.8 (Figure 5). The shallow depth of nearly pure groundwater at the Lost River sites in the early 1980s corresponds to the shallow penetration of bomb recharge reported by Gorham and Hofstetter

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[1971] for the Red Lake II bog in the 1960s (Figure 5) despite the distance (36 km) and sampling time (11 years) that separate these measurements.

5.3.1 Binary-Mixing Models (1969-1983)

A 2-component mixing model was used to estimate the fraction of recharge that was added to pore waters during the peak of the bomb period at the Red Lake II bog (Figure 5). A tritium concentration of 86 or 178 $TU_{cor2008}$ was used as the extreme end member for bomb-peak fallout in this region [*Stewart and Wyerman*1970] and 0.05 $TU_{cor2008}$ as the end member for pre-bomb pore waters. Based on these end members, the model shows a rapid decline in bomb-peak tritium with depth at the Red Lake II bog in 1965-1969. The bomb signal declined from 1) 25-to-50% at 18 cm, 2) 15-to-30% at 120 cm, 3) 3-to-7% at 180 cm, 4) 2-to-4% between 320-350 cm, and 5) less than 1% below 350 cm assuming bomb-peak values of 86 and 178 $TU_{cor2008}$ respectively (Figure 5). In addition, this mixing model indicates that a small fraction of bomb water had penetrated down into the deepest portion of the peat profile in 1969 less than 5 years after the peak in bomb fallout and 14 years after the onset of nuclear weapon testing in the atmosphere. However, the model also shows that the bulk of the bomb-tritium signal remained in the upper meter of the peat profile through the 1960s [*Gorham and Hofstetter*, 1971]. After 1971, the mixing relationships for tritium became too complex in the GLAP pore waters to be treated effectively with a simple binary mixing model.

Binary mixing models for pore-water Ca^{++} also indicate the shallow penetration of recharge at the Lost River peatland from 1981 through 1983 (Figure 5). Using 2 mg l^{-1} as the endmember for precipitation and only 20 mg l^{-1} as the endmember for groundwater the model indicated that the mixing zone between groundwater and recharge was largely confined to the upper meter of the peat profile at this time. Below 100 cm the mixing models indicate that 90% or more of the pore waters were derived from groundwater that was transported upward from the underlying mineral substratum.

5.4 Pore-Water Geochemistry: 1990-2008

By 1997, bomb tritium had dispersed throughout the entire peat profile at all the bog and fen sites across the GLAP (Figure 6). Tritium concentrations generally ranged from 6.2 to 18.1 $TU_{cor2008}$ in most of the pore-water profiles collected between 1997 through 2008 [*Rivers,*

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1999*; Dasgupta*, 2010]. Most of these values remained within the limits expected for post-bomb recharge with respect to the Ottawa record. The few exceptions were a) four samples with a slightly higher concentration (21.0 to 28.5 $TU_{cor2008}$) and b) several samples with concentrations below 6 $TU_{cor2008}$ (grey vertical line in Figure 6). As a result there was no unequivocal evidence for recharge dating from either the bomb peak or pre-bomb periods. If tritium was still present from these periods it had become too diluted with pre- or post-bomb recharge to be clearly distinguishable.

The cation profiles from this period (Figure 7) had changed dramatically from those of the early 1980s (Figure 5). This switch indicates that recharge with the chemical signature of precipitation had moved much deeper within the peat profile by 1990 and had largely flushed the pore waters within the upper 220 cm of all bog and fen sites (Figure 7). One noteworthy feature of these cation profiles was their relatively coherent concave shapes in both bog and fens across the entire GLAP despite local variations in their hydrogeologic settings [*Glaser et al.*,1997]. Cation concentrations in fens, however, remained significantly higher at any given depth interval than those in raised bogs. This pattern remained relatively stable throughout subsequent sampling periods except that the pore waters tended to become slightly more dilute at any given depth from 1990 to 2008 (Figure 7). Further evidence for the deep penetration of recharge is provided by the evaporative enrichment of $\delta^{18}O$ in the deepest pore waters of fen water tracks across the GLAP in 2010 at sites where water ponded above the land surface [*Levy et al.*, 2014].

A binary-mixing model provides further evidence that downwardly moving recharge dominated the pore waters to a depth of 220 cm below which the recharge waters were progressively mixed with an increasing fraction of geogenous groundwater (Figure 7). This interpretation is supported by tritium and calcium profiles from the Red Lake II bog in 1997 and 2008 (Figure 8). The steep decline in tritium concentrations below a depth of 220 cm corresponds to the increasing concentration of Ca indicating greater dilution of post-bomb recharge by pre-bomb groundwater.

Both the tritium and cation profiles remained remarkably stable within the bogs and fens of the GLAP over multi-decadal timescales despite local variations in peat depth, landform size, and hydrogeologic setting (Figures 5- 8). For example, there was little variation in the tritium or calcium profiles from the Red Lake II bog between 1997 and 2008 once the tritium values

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were normalized for radioactive decay to a common end point of 2008. The principal exception was a major shift in the pore-water chemistry that occurred between the 1983 and 1990 sampling periods (Figures 5-8).

5.4 Pore-Water Biogeochemistry (1991-2008)

Two isotopic tracers provide evidence for high rates of methanogenesis throughout the peat profiles of the bogs and fens of the GLAP during the 1991 through 2008 sampling periods. Dissolved inorganic carbon (DIC) was significantly enriched in $\delta^{13}C$ reaching values as high as 10‰ in bog and about 6‰ in fen profiles relative to the $\delta^{13}C$ signatures of biomass (-27‰), atmospheric CO_2 (-8‰) and DIC in groundwater (-11‰) (Figure 9). Methanogenesis is the only biogeochemical process that could produce such an enrichment effect because the CO_2 that is co-produced with the depleted $\delta^{13}CH_4$ must be enriched in ^{13}C in order to maintain isotope mass balance with respect to the original carbon source [*Corbett et al*., 2013b, 2015). This enrichment effect was greater in forested bogs (e.g. Red Lake II bog crest) than in sedge-dominated rich-fens (e.g. Red Lake II fen, RL I fen) during the 1997-1997 and 2007-2008 sampling periods (Figure 9) [*Chasar* 2000a; *Corbett et al* 2013b].

Methane was significantly enriched in $\Delta^{14}C$ within the pore waters of bogs and fens relative to that of the solid-phase peat at any given depth interval (Figure 10A). This offset in radiocarbon activity indicates that methanogenesis was fueled in part by labile DOC that was transported downward from the rhizosphere to the deeper portions of the peat deposits of the GLAP [*Chanton et al.* 1995; *Chasar* 2000a, 2000b; *Glaser and Chanton* 2009*; Corbett et al.* 2013a, 2015]. Methane from the pore waters of sedge fens (e.g. Red Lake II fen) had consistently higher $\Delta^{14}CH_4$ values than those of forested bogs (e.g. Red Lake II bog) at any given depth interval (Figure 10A). The $\Delta^{14}CH_4$ values were highest in the near-surface peat of all sites and then declined with increasing depth. In addition, a binary mixing model (Eq. 2) provides strong evidence that the fraction of recently-fixed carbon in methane samples from sedge-fen profiles increased significantly across the GLAP from 1991 to 2008 (Figure 10B).

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Two ombrotrophic bog sites provide further evidence for the importance of sedge vegetation on the radiocarbon content of pore-water methane (Figure 11A). Methane was significantly more enriched in $\Delta^{14}C$ in the pore waters of a bog drain site, which is dominated by sedges than in the pore waters under the adjacent forested crest (Figure 11A). However, sedge fens located within a persistent discharge zone for groundwater such as the spring-fen channel at Lost River (site c in Figure 1) have much lower $\Delta^{14}CH_4$ values than those of other sedge fens (Figure 11B).

6. Discussion

Northern peatlands are concentrated in regions that have warmed substantially over the past 800 years and this trend has recently accelerated in step with the steep rise of greenhouse gases in the atmosphere since 1920 AD [*Overpeck et al*., 1997; *IPCC,* 2013]. Although continued warming may eventually destabilize the carbon pool in northern peatlands it remains uncertain how changing climatic patterns regulate the conversion of solid-phase peat into volatile greenhouse gases that can be emitted to the atmosphere [*Blodau 2002*]. Three different approaches have been reviewed by Bridgham et al. [2013] to elucidate this problem: a) comparative studies that measure methane emissions across distinct climatic or ecological gradients, b) experimental manipulations of peat mesocosms or field sites to mimic the effects of climatic warming, and c) process-based models that simulate the effects of climate change on idealized model systems. A common simplifying assumption that is often adopted by many of these studies is that methane production is confined to the near surface layers of a peat deposit by the availability of labile carbon substrates.

The Glacial Lake Agassiz peatlands in northern Minnesota offers an unusual opportunity to combine several of these separate approaches into a single, integrated, long-term investigation. The large raised bogs and fen water tracks in this region have developed across a steep climatic gradient providing the basis for a comparative analysis of climate-carbon-water interactions, whereas changing precipitation patterns on different timescales simulate an experimental manipulation of the entire regional ecosystem without creating unintended artifacts. Moreover, the very low degree of regional variability of the different bog and fen landforms across the GLAP [*Glaser,* 1992a*; Glaser et al.,* 1987] provides a reliable means for scaling up local site measurements to the level of the regional landscape. Finally, the

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hypothesis that methane production is driven by the supply of labile DOC produced near the peat surface provides an opportunity to analyze the linkage of precipitation patterns to the vertical transport of labile DOC and methane production in these peat deposits.

6.1 Pore-Water Chemistry

The GLAP pore waters were consistently stratified into three discrete zones based on their chemical properties: a) an upper zone of dilute pore water similar to that of recent precipitation, b) a deeper zone with cation concentrations more typical of geogenous groundwater within calcareous till, and c) a middle mixing zone that forms a transition between these upper and lower layers. The depth profiles for cations were remarkably similar from an array of sites on decadal timescales despite local changes in peat depths, landform size, and hydrogeologic setting (Figures 5 and 7). The regional stability and coherence of these chemical profiles over multi-decadal timescales provides credence to the robustness of the entire sample set despite its limited sample size (especially prior to 1990) and widely spaced sampling intervals.

The pore-water profiles from the GLAP appear to represent varying mixtures of precipitation and groundwater based on the nearly linear relationships among the major inorganic constituents [*Glaser et al*., 1981, 1990, 1997; *Siegel and Glaser*, 1987; *Siegel et al.*, 1995]. One of the few departures from this general relationship involves DIC and CH_4 that can be produced within the peat profile by anaerobic microbes [e.g. Figure 6c in *Glaser et al.*, 1997]. Two distinct solute transport regimes can be defined on the basis of binary-mixing models: a) a shallow recharge regime that prevailed during the intermittent dry-to-moist phase from 1965 through 1983 and b) much deeper recharge during the moist phase between the 1990 to 2008 sampling periods.

Prior to 1984 pore-water profiles were only available from the 160-km^2 Red Lake II bog complex [*Gorham and Hofstetter*, 1971] and the much smaller 20-km^2 Lost River peatland [*Siegel and Glaser*, 1987]. Nevertheless, the tritium profiles reported from the Red Lake II bog in 1965-1969 closely corresponded to the cation profiles reported from the Lost River sites in 1981-1983 (Figure 5). These profiles indicate that only the upper meter of the peat profile was largely flushed by downwardly moving precipitation (i.e. recharge) at this time, whereas the deeper pore waters retained a chemical signature diagnostic of groundwater.

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However, by 1990 the cation profiles had shifted from a convex shape indicative of shallow recharge to the concave shape indicating much deeper recharge by precipitation in all the bog and fen sites (Figures 7 and 8).

Binary mixing models provide further evidence that the pore waters were representative of varying mixtures of contemporary precipitation (^{3}H >1 TU; Ca concen. < 2 mg l^{-1}) and geogenous groundwater (^{3}H <<1 TU; Ca concen. >2 mg l^{-1}). Prior to 1990, the mixing interface between contemporary recharge (from precipitation) and nearly pure groundwater was located at 100 cm depth below the water table (Figure 5). However, by 1990 nearly pure recharge had largely flushed the pore waters to a depth of 200 cm, below which there was a gradual increase in the fraction of groundwater (Figures 7 and 8). The close agreement between the ^{3}H and Ca profiles was particularly evident at the Red Lake II bog crest where the sharp decline in post-bomb tritium below 250 cm was matched by the corresponding increase in Ca concentrations above 4 mg l^{-1} (Figure 8A and 8B).

The depth of the mixing zone between the downward and upward transport systems apparently stabilized after 1990 except for a slight enrichment with recharge from precipitation between 1991 to 2008 at each sampling depth. The abrupt shift in the pore-water chemistry between 1983 and 1990 across the GLAP therefore seems to represent a regional perturbation of regional transport systems by a climatic shift or some other external driver.

6.2 Transport Processes

Gorham and Hofstetter [1971] originally inferred that advective transport was limited to the near-surface layers of the Red Lake II bog in the 1960s by the low permeability of the deeper peat. The deeper penetration of bomb tritium was therefore assumed to be driven solely by molecular diffusion. However, several difficulties arise when trying to fit their reported tritium profiles to Fickian Diffusion [*sensu Ingerbritsen et al.*, 2006]. Binary-mixing models indicate that a very small but significant fraction of bomb tritium had penetrated downward to reach the basal peat by 1969. This migration rate of 3-4 m in only 15 years since the onset of the bomb era is too rapid to be driven solely by molecular diffusion given the likely diffusion coefficients of 10^{-7} cm^2 s^{-1} or lower in porous media [*Freeze and Cherry*, 1979; *Ingebritsen et al.*. 2006]. In addition, by 1997, contemporary recharge enriched by bomb tritium had

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partially flushed the entire peat profile at all sites leaving no unambiguous trace of recharge from the pre-bomb (<1950) or bomb peak (1954-1970) eras.

In contrast, Siegel and Glaser [1987] identified advection as the principal mode of solute transport in the Lost River peatland during the early 1980s. The deeper peat imposed no apparent barrier to vertical transport at this site since Chason and Siegel [1986] reported relatively high values for the in situ vertical hydraulic conductivity (10^{-3} to 10^{-5} m s^{-1}) throughout the peat profiles of the bog, fen, and spring fen sites. Moreover, the vertical hydraulic head gradients exceeded several centimeters per meter, which combined with the measurements for hydraulic conductivity indicate significant vertical flow velocities within all of these peat landforms [*Siegel and Glaser,* 1987]. The chemical composition of the pore waters provided further evidence for the upward transport of almost pure groundwater to a depth of only 1 m, above which the pore waters became progressively diluted by downwardly moving precipitation (Figure 5), [*Siegel and Glaser,* 1987].

Both the tritium and cation profiles provide firm evidence for the existence of dual transport systems within these peat deposits: a downward component derived from precipitation falling on the peat surface and an upward component arising from the underlying mineral groundwater system [*Romanowicz et al.,* 1993*; Siegel et al.,1995; Glaser et al*., 1997]. These transport systems could only be driven by advection or transverse dispersion [*Reeve et al.,* 2000, 2001] since molecular diffusion would be too slow to account for the rapid downward penetration of bomb tritium or the abrupt shift in the cation profiles between the 1983 and 1990 sampling periods. In addition, the measured vertical-hydraulic head gradients [*Siegel and Glaser,* 1987*; Rosenberry et al.,* 2003] are too high to permit pure diffusive transport, which only prevails when the hydraulic gradient is 0.001 or lower [*Fetter,* 1999*; McKenzie et al.* 2002]. The major shift in the pore-water chemistry in the late 1980s most likely represented a region-wide shift in groundwater flow systems that strengthened the downward transport component, while weakening upward fluxes from the underlying glacial deposits.

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6.3 Climate Drivers for Flow Regimes

Groundwater flow systems appear to be sensitively adjusted to the relatively dry regional climate in northwestern Minnesota. The mean value for precipitation was only 558 mm yr^{-1} from 1895 to 2008, which is close to the lower limit needed to maintain a high water table within both bogs and fens [*Kivinen & Pakarinen,* 1981*; Glaser et al.* 1997]. Further moisture stress was produced by the abrupt shifts between moist and dry periods, which occurred on seasonal, sub-decadal, and multi-decadal timescales (Figure 2). The multi-decadal shifts in precipitation in particular perturbed groundwater flow systems across the GLAP producing distinct changes in hydraulic head gradients and pore-water chemistry.

Shifting precipitation patterns during the Transitional Dry-to-Moist Period (1941-1986) were probably responsible for the sharp reversals in hydraulic head that were first observed seasonally in the Lost River peatland in the early 1980s [*Siegel and Glaser,* 1987] and later inter-annually across the entire GLAP from 1990 to 1991 *[Romanowicz et al.,* 1993*; Glaser et al.,* 1997]. Lower water tables during the dry years probably allowed geogenous groundwater to rise higher into the peat profile, whereas rising water tables during the intervening wet years strengthened downward transport. However, the available chemical profiles indicate that the balance between these opposing transport systems was apparently still shifted toward upward transport during the Transitional Dry-to-Moist Period at least until the 1983 sampling period at Lost River. The high elevation of geogenous groundwater in the peat profiles of the GLAP from 1965-1983 may therefore represent a lingering legacy effect of the extremely dry decades of the 1920s and 1930s that depressed water levels across the entire region.

In contrast, there was only one major shift in the solute profiles in both bogs and fens during the 43-year time series. This shift in cation profiles occurred abruptly between the 1983 and 1990 sampling periods when the cation profiles changed from the convex shape typical of shallow recharge to the concave profile characteristic of much deeper flushing by recent recharge. The rapid rate of this shift is unexpected because advective-dispersive simulation models predict it would take a decade of continuous recharge to change the pore-water chemistry within the Lost River bog from a convex to a concave profile [*Siegel et al.,* 1995]. Although this shift occurred toward the end of the Transitional Dry-to-Moist Period (1942-1992), its relationship to climatic drivers is not clear. It could represent: 1) the cumulative

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effect of frequent flow reversals from 1942-1990 followed by a long period of persistent downward transport after 1990, 2) the disruption of a hydraulic confining layer composed of trapped gas bubbles at 1-m depth [*Romanowicz et al.,*1995*; Rosenberry et al*., 2003*; Glaser et al,,* 2004c], or 3) the effect of some non-climatic threshold related to the intrinsic permeability of the peat fabric, such as the dual porosity of peat deposits and matrix diffusion [*Ours et al*. 1997*; Hoag and Price,* 1997; *Rezanezhad et al.* 2012*; Blodau and Moore,* 2002*; Levy* 2012]

6.4 Climate Drivers for Methane Production and Storage

Both field and laboratory studies indicate that methane production is dependent on the quality and quantity of organic substrates in anoxic peat profiles [*Segers,* 1998*; Blodau,* 2002*; Christensen et al.,* 2003*; Nilsson and Öquist,* 2009*; Bridgham et al*., 2013]. It has therefore been widely assumed that rates of methane production are greatest in the uppermost layers of peatlands in which the peat contains a high fraction of labile carbon compounds [*e.g Clymo* 1984]. According to this conceptual model methane production would be modulated by a) water-table fluctuations that determine the depth of the aerobic zone and boundary between aerobic and anaerobic metabolism [*e.g. Moore and Roulet,* 1993] and b) changes in temperature, which influence rates of biochemical reactions and also the depth of the unfrozen active zone in permafrost regions [*e.g. Davidson and Janssens,* 2006; *Blodau et al.,* 2007; *Bridgam et al.,* 2013].

However, anaerobic decomposition pathways in bogs and fens are primarily fueled by dissolved forms of labile carbon substrates and these solutes can be transported downward from their production zones near the peat surface to the basal peat. A close linkage should therefore be expected between metabolic pathways that are substrate dependent, such as methanogenesis, and solute transport systems in peat deposits. This hypothesis can be tested by the 43-year dataset of pore-water chemistry and the carbon isotopic signatures of DIC and CH_4 across the bogs and fens of the GLAP.

The shallow recharge systems that prevailed during the Transitional Dry-to-Moist Period (1941-1986) would have limited the downward transport of labile DOC to the upper meter of the peat profile. At deeper depths methanogenesis would have been increasingly limited to carbon substrates that could be extracted from the solid-phase peat. The peat, however,

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should become increasingly refractory at progressively deeper depths and longer exposure time to microbial decay. Although methane profiles were not measured during that period, indirect evidence supports this hypothesis. Siegel and Glaser [*1987*] reported persistent zones of overpressure at 1-m depth in the Lost River peatland that were most likely sustained by the production of gas bubbles trapped under shallow hydraulic confining layers [*sensu Rosenberry et al.,* 2003*; Glaser et al.,* 2004c]. No evidence for deeper gas pockets were apparent from 1981 to 1983 at Lost River or at other sites across the GLAP.

The shift to a moister climate after 1990 strengthened downward transport across the GLAP driving labile DOC deeper within the peat profile where it could stimulate methanogenesis. Overall, dissolved methane concentrations increased with depth, from 1990 to 2008 with concentrations in the deeper peat (1-4 m) exceeding those in the near-surface horizons (0-1 m) by 2-to-4 times [*Romanowicz et al.,*1993*, 1995; Glaser et al.,* 1997*; Chasar* 2000a, 2000b*; Corbett,* 2012]. Rates of methanogenesis were sufficiently high during this period to produce large volumes of free-phase gas within the deeper peat [*Rosenberry et al.,* 2003*; Glaser et al.,* 2004c; *Parsekian et al.,* 2010, 2011*; Reeve et al.,* 2013] that episodically escaped through ruptures in hydraulic confining layers [*Rosenberry et al.,* 2003*; Glaser et al., 2004c; Reeve et al.,* 2013].

High rates of methanogenesis during the 1997-2008 sampling periods are also indicated by the enrichment of the deeper δ^{13}C-DIC pool to values approaching +6‰ in fens and +10‰ in bogs. These values represent a large isotopic enrichment over background levels of δ^{13}C-DIC derived solely from atmospheric CO_2 (-8‰), bicarbonate in groundwater (-11‰), or the decomposition of soil organic matter by non-fractionating pathways (-27‰). Methanogenesis is the only metabolic process capable of producing such a large kinetic fractionation effect in freshwater peatlands since both aerobic respiration and fermentation of dissolved organic matter are non-fractionating [*Chasar et al.,* 2000a*; Hornibrook et al.,* 2000; *Steinmann et al.,* 2008*; Corbett,* 2012; *Corbett et al.,* 2013b, 2015].

The end products of anaerobic metabolism in freshwater peatlands result in the production of one mole of $\sum CO_2$ for every mole of CH_4 (*Megonigal et al.,* 2003; *Steinmann et al.,* 2008; *Corbett et al.,* 2013b]. During this process the surrounding δ^{13}C-DIC pool becomes heavier as methanogens preferentially reduce isotopically lighter CO_2 to CH_4 via the carbonate

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reduction pathway or release isotopically heavier CO_2 as an end product of the acetate cleavage pathway. However, the δ^{13}C-DIC pool also evolves as this isotopically heavier δ^{13}C-DIC pool mixes with lighter δ^{13}C-DIC derived from other sources. The substantial increase in δ^{13}C-DIC values from 0 to 150 cm depth, for example, most likely occurs as isotopically heavier δ^{13}C-DIC produced by methanogenesis mixes with lighter δ^{13}C-DIC transported downward from the atmosphere or near-surface zone of aerobic decomposition. Furthermore, the consistently lighter δ^{13}C-DIC profiles in fens relative to that of the bogs is most likely a reflection of the greater flushing of the fen pore waters by either downward transport of biogenic DIC from aerobic heterotrophic and autotrophic respiration or abiogenic DIC transported upward from the underlying groundwater system.

At deeper depths δ^{13}C-DIC values appear to approach a steady state maintained by a dynamic balance among 1) rates of methane production, 2) solute transport processes, and 3) residence times of DIC. Rates of methanogenesis should be limited at deeper depths by a decreasing supply of labile DOC transported downward from higher strata. In addition, any rise in δ^{13}C-DIC values will be buffered at deeper depths by increased mixing with isotopically lighter DIC transported upward from the mineral substratum.

Finally, ebullition fluxes will prevent the continual buildup of the isotopically heavier DIC produced by methanogenesis. Once a methane bubble forms, other gases will diffuse into it lowering the equilibrium saturation concentration of every gas in solution. The loss of gas bubbles as ebullition proceeds should then stabilize the isotopic mixture within the DIC pool since phase changes are not associated with isotope fractionation of dissolved gases [*Chanton,* 2005]. The δ^{13}C-DIC profiles in the bogs and fens of the GLAP are therefore indicative of relatively high rates of methanogenesis throughout the entire peat profiles from 1997 through 2008.

The close linkage of methane production to solute transport systems is most clearly shown by the radiocarbon signatures of CH_4 [*Chanton et al.,* 1995, 2008*; Corbet et al.,* 2013a]. The $\Delta^{14}CH_4$ profiles in bogs and fens were significantly enriched in Δ^{14}C relative to that of the solid-phase peat at any given depth during the 1991 through 2008 sampling periods (Figures 10A). This large enrichment effect is indicative of the downward transport of recently-fixed DOC from near-surface production zones. The reactivity of this DOC is apparently greater

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under sedge-dominated sites (e.g. RLII fen and RLII bog drain) than at sites dominated by woody plants (e.g. RLII bog crest) regardless of the relative abundance of *Sphagnum* (Figure 11) [*Chanton et al.,* 2008]. Although the shift to deeper recharge stimulated methane production throughout the profiles of bogs and fens after the late 1980s, this effect was greatest in peatland sites dominated by sedges (Figure 10 and 11).

6.5. Climate-Driven Shifts in Methane Production Zones and its Broader Significance

The peak production zones for methane apparently doubled in thickness across the GLAP after the shift to a moister climate (1990-2008) strengthened downward transport systems and increased the supply of labile carbon substrates within the deeper peat. This conclusion is supported by several lines of evidence. Prior to 1990 it would have been implausible if not impossible for recently-fixed DOC to be transported downward in sufficient quantities to stimulate methanogenesis within the deeper peat given the shallow recharge systems that prevailed across the GLAP during this drier period. In contrast, the region-wide shift to deep recharge after 1986 was responsible for transporting labile DOC much deeper into peat profiles. The isotopic profiles for $\Delta^{14}CH_4$ provide firm evidence for the preferred uptake of these recently-fixed carbon substrates throughout the peat profiles of bogs and fens but the stimulating effect of recently-fixed DOC was significantly greater in the pore waters of sites dominated by sedges.

The principal exception to this pattern is the Lost River spring fen (site c in Figure 1), which is located within a persistent zone for groundwater discharge [*Glaser et al.,* 1990; *Romanowicz,* 1993]. Upwelling groundwater creates an hydraulic barrier to the downward transport of recently-fixed DOC, precluding its capacity to stimulate methanogenesis within the deeper peat. This conclusion is supported by the near absence of an isotopic fractionation signal in the δ^{13}C-DIC profile of the spring fen that ranged from -12.1‰ at 0.5 m depth to -14.3‰ at 2.2 m [*Chasar,* 2002]. It is therefore noteworthy that the cation profiles from this site retained the convex shape that was once typical of bogs and fens across the GLAP during the Transitional Dry-to-Moist Period [e.g. *Rivers,* 1999]. Little stimulation of methanogenesis by labile DOC would therefore be expected in the GLAP during this period.

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The 43-year dataset from the GLAP provides a different perspective on the division of peat profiles into two separate compartments that are decoupled with respect to their hydrology and biogeochemistry. Chemical tracers indicate that the entire peat profile within the GLAP is transmissible to fluids and solutes that move either upward from the mineral substratum or downward from the peat surface. The shifting strength of these converging transport systems determines the relative thickness and depth of the chemical zones, which stabilize over multi-decadal timescales until being offset by a a long-term shift in climate (Figure 12). The tracers also show that labile DOC can move downward and transform deeper peat strata into active production zones for greenhouse gases during long moist periods. Although the pore-water chemistry within the GLAP currently conforms to a 3-layer model suggested by Morris and Waddington [2011] the stability and distribution of these zones are dependent on the regional precipitation regime and elsewhere by the local hydrogeologic setting.

The GLAP model for solute transport and methane production is applicable to a wide range of peatlands from other regions. Similar cation and methane profiles were reported from the bogs, fens, and spring fens across a 24,000 km^2 study area in the southern Hudson Bay Lowland [*Reeve et al*., 1996; *Glaser et al*., 2004a]. Further evidence for deep advective transport of solutes has also been reported for a small peatland from New York State [*McNamara et al.*, 1992] a raised bog in Maine, USA [*Reeve et al*., 2009], and a tropical peat dome in Brunei in northern Borneo [*Hoyt et al*., 2014]. In addition, Charman et al. [1994; 1999] presented evidence for the deep penetration of bomb-tritium and the uptake of recently-fixed carbon by methanogens to depths of 170 cm from a continental peatland in eastern Canada (Wally Creek Watershed) and 250 cm from an oceanic peatland (Dartmoor) in the United Kingdom. All of these studies used piezometers to sample pore waters from different depth intervals within peat profiles similar to the methodology employed in the GLAP.

In contrast, pore-water datasets more supportive of the Ingram-Clymo model of a quasi-closed deep peat layer were based on incubation studies, model simulations, or pore-water samples collected with custom sampling devices. The general conclusion of these studies is that solute transport is restricted to molecular diffusion in the deeper peat [*Clymo and Pearce,* 1995*; Steinmann and Shotyk,* 1997; *Steinmann et al.,* 2008*; Beer and Blodau,* 2007*; Beer et al.,* 2008; *Clymo and Bryant,* 2008] and methanogenesis is limited in deep peat by the increasing fraction of recalcitrant organic substrates.

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These contrasting viewpoints may be the result of differences in sampling methods, source vegetation for DOC, climatic conditions, or the local hydrogeologic setting. Piezometers, for example probably sample a larger Representative Elemental Volume [sensu *Bear*, 1972] than that of the custom samplers used in many biogeochemical studies. As a result, piezometers are more likely to draw pore waters from nearby macropores in which the bulk of fluid and solute transport occurs in porous media [e.g. *Bear*, 1972; *Ingebritsen et al*., 2006], whereas the custom samplers are better suited to tap diffusive transport from the dead pore space in direct contact with the sampler ports. Methane production could be much lower in the dead pore space than within pores in close contact with macropores as shown by the incubation studies of Corbett et al. [2015].

The diverging interpretations of peatland hydrology and biogeochemistry provide different insights on the scale-dependent processes that govern solute transport and methane production within heterogeneous peat profiles. Nevertheless, methane production rates are sufficient to produce large volumes of free-phase gas in the deep peat (>150 cm) of the GLAP [*Rosenberry et al.,* 2003; *Glaser et al.,* 2004c*; Paresekian et al.,* 2010, 2011] and other [*Comas et al.,* 2005, 2008; *Strack and Mierau.* 2010] but apparently not all [*Clymo,* 2015] boreal peatlands. The role of the deeper peat as an incubator of greenhouse gases may vary globally given the substantial differences that exist with respect to sampling periods and regional climatic conditions. Locally, the hydrology and biogeochemistry of peat deposits can also be affected by differences in the hydrogeologic setting, source vegetation for DOC, hydraulic properties of the peat itself, and the magnitude of human disturbance.

Nevertheless the deeper portions of peat deposits remain a potentially large and under-studied source for the greenhouse gases under a moist climatic regime. The importance of deep peat profiles as a potential incubator for methane is demonstrated by the 43-year record of pore-water analyses from the GLAP. Not only does this record extend over a sufficiently long period to span a multi-decadal shift in the regional climate, but it also tracks changes in the chemistry of the deeper pore waters from an array of peatland types using multiple chemical and isotopic tracers.

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7. Conclusions

Future changes in climate are expected to have the greatest impact on the near-surface layers of peatlands by changing water levels and peat temperatures [*Roulet et al.* 1992; *Moore et al.* 1998; *Davidson and Janssens*, 2006]. However, a 43-year record of the pore-water chemistry from a major peat basin provides an expanded perspective on the linkage of climate change to solute transport and methane production in deep peat profiles. Tritium and cation tracers indicate that contemporary recharge only flushed pore waters in the upper meter of a peat profile during a multi-decadal drier period. This transport regime partially corresponds to the assumptions of the acrotelm/catotelm model of peatland hydrology originally conceptualized by Ingram [1983] and Ivanov [1983]. In contrast, progressively moister conditions after 1991 strengthened downward transport across the GLAP thereby increasing the delivery of labile carbon substrates to the deeper anaerobic peat of both bogs and fens. This climatically driven shift in solute transport regime apparently doubled the peak production zones for methane and also converted the entire peat profile into an incubator for methane as indicated by the carbon isotopic profiles. These data suggest that methane production in northern peatlands may be more sensitive to future changes in precipitation than temperature alone over multi-decadal timescales.

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Figure 1

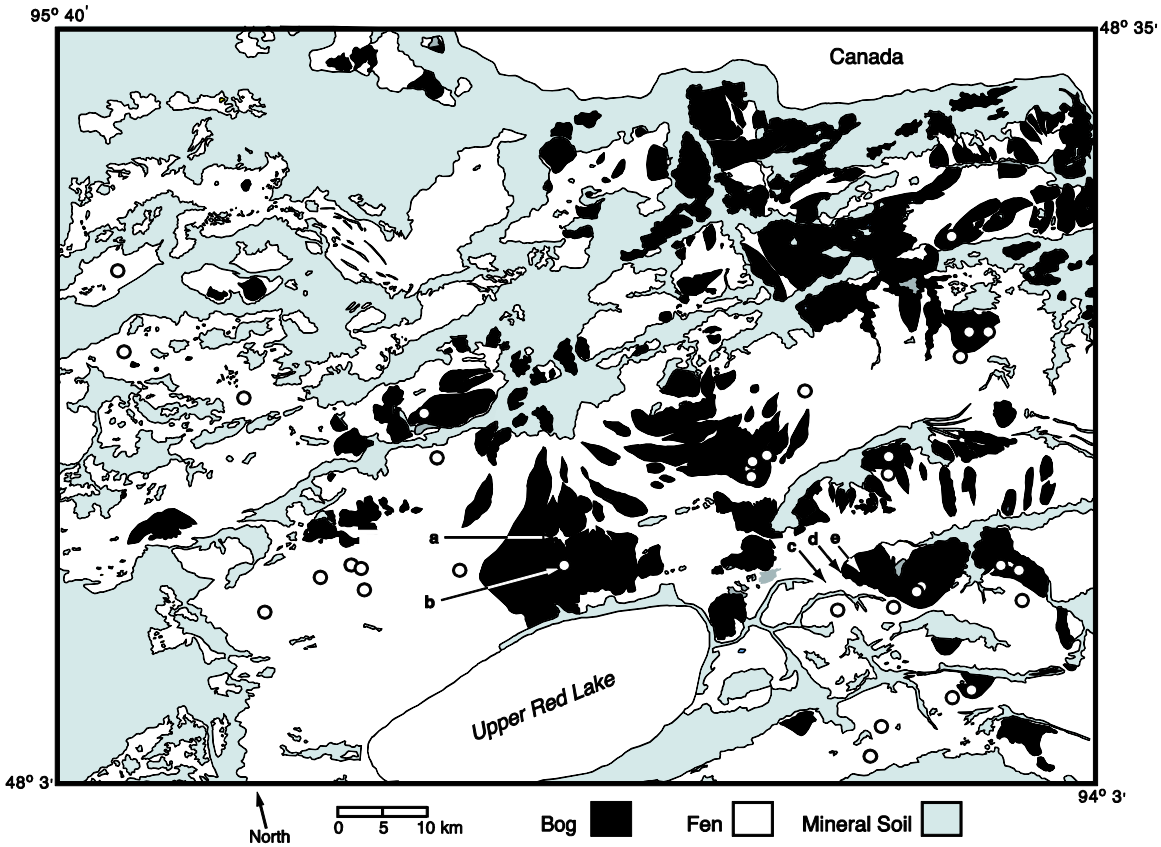

Figure 1. Map of the Glacial Lake Agassiz peatlands, northern Minnesota. The locations marked are the Red Lake II fen (a), Red Lake II bog (b), Lost River spring fen (c), Lost River fen water track (d), and Lost River bog (e). The other sampling locations for pore-water chemistry are marked by circles. The geographic coordinates of all sites are presented by Siegel and Glaser [1987], Romanowicz [1993] and Glaser et al. [1997].

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Figure 2

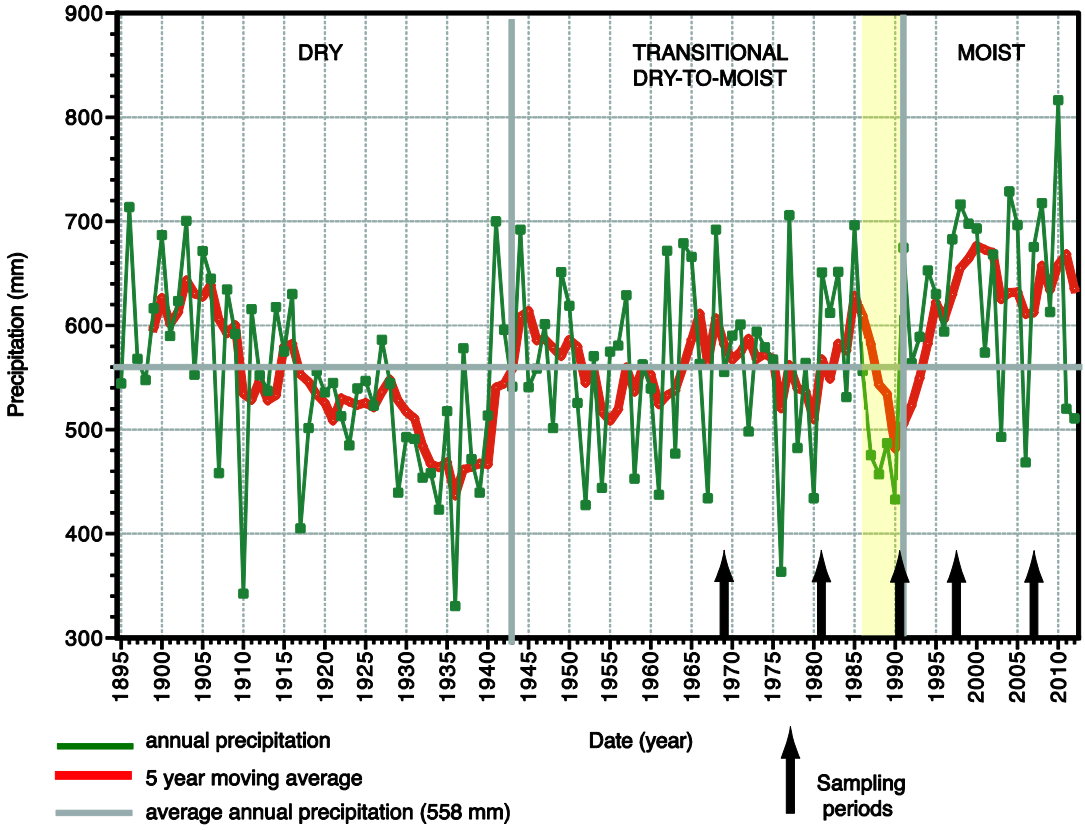

Figure 2. Precipitation record for northwestern Minnesota (1895-2012). The plot shows the average annual precipitation (green line and solid boxes), the 5-year moving average of these values (red line and open diamonds), and the median average value (horizontal grey line) for the 117-year record. Also marked are the three climatic phases (vertical grey lines), and 5 main sampling periods (vertical arrows). The diffuse transition at the end of the Transitional Dry-to-Wet Period is marked by the yellow column.

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Figure 3

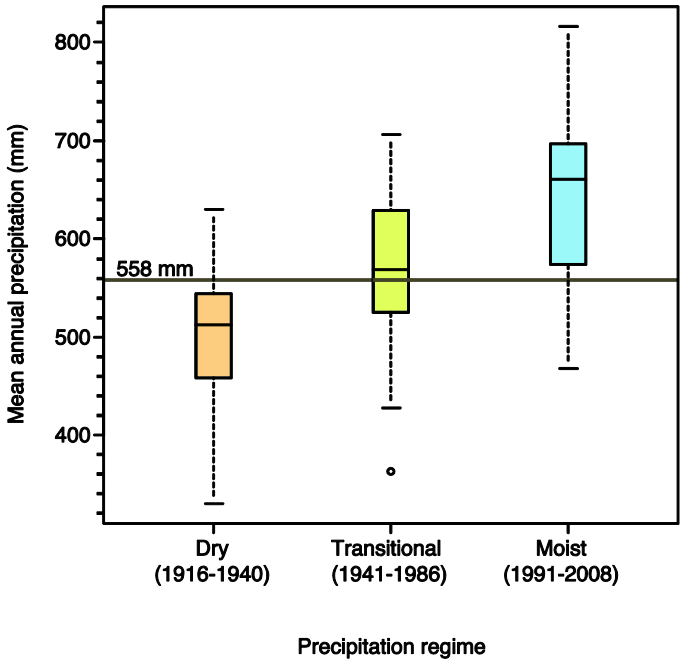

Figure 3. The distribution of mean annual precipitation in northwestern Minnesota from 1916 to 2008. relative to the long-term average of 558 mm yr^{-1} from 1895 to 2008. The boxes are bounded by the upper (75%) and lower (25%) quartiles and enclose a horizontal band marking the median of the distribution. The whiskers define 1.5 times the quartile range and outliers are marked by circles.

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Figure 4

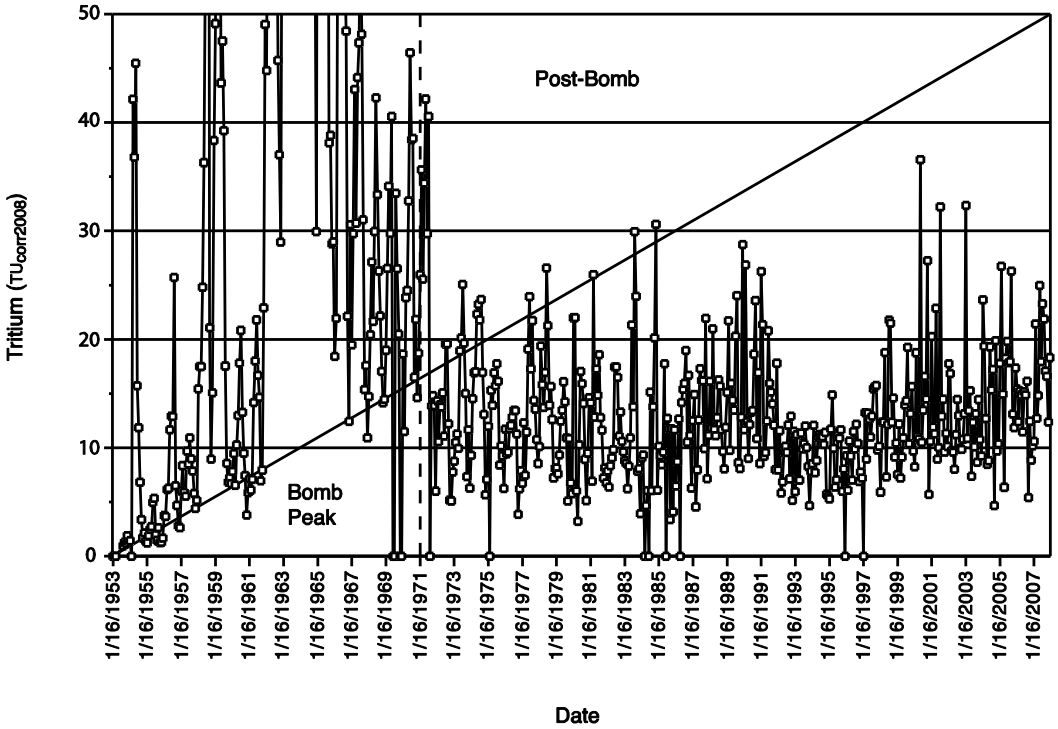

Figure 4. Normalized values for the Ottawa Canada record for tritium in precipitation. All tritium values are corrected for radioactive decay through 2008 to provide a uniform standard of comparison across the entire time series. The dashed line divides the curve into the bomb-peak and post-bomb intervals. The y axis is truncated above to prevent peak tritium concentrations during the 1960s from obscuring the trends in tritium fallout after 1970.

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Figure 5

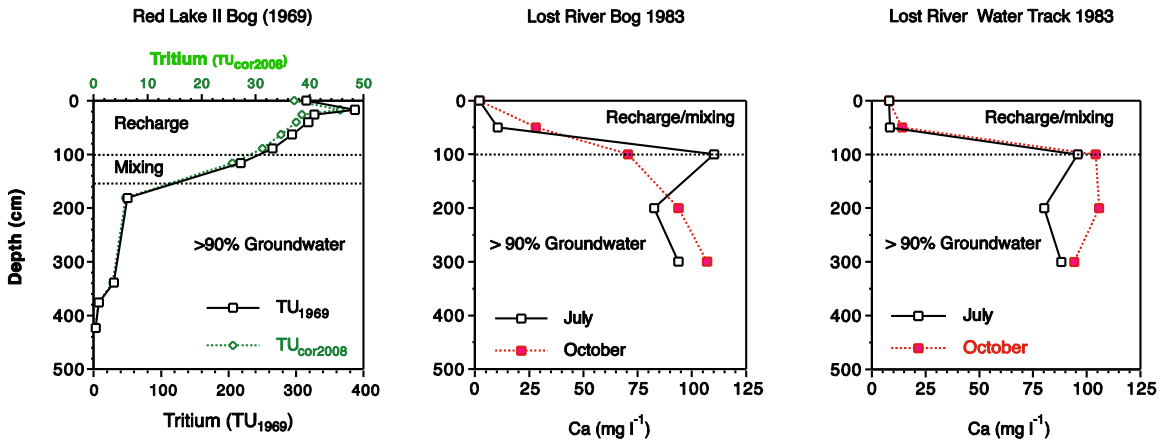

Figure 5. Tritium profiles from the Red Lake II bog (1969) [*Gorham and Hofstetter*, 1971] correspond with cation profiles from Lost River bog and fen (1983) [*Siegel and Glaser*, 1987]. Note the different color-coded scales for tritium on the upper and lower x axis (left panel).

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Figure 6

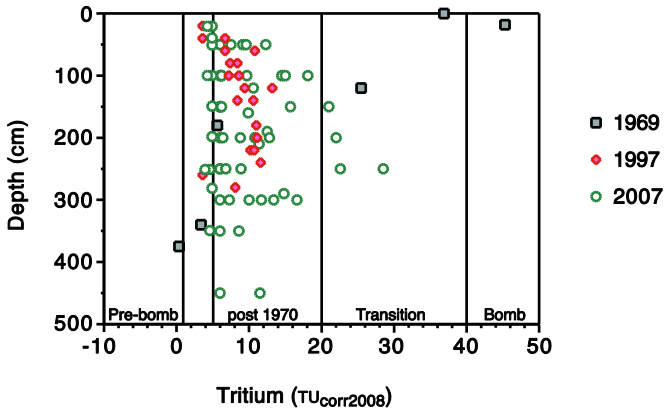

Figure 6. Tritium profiles collected across the GLAP from 10 bogs and fens during 1969, 1997, and 2007. All tritium values are transformed for radioactive decay through 2008 and fall within ranges corresponding to the pre-bomb (<1953), bomb peak (1954-1970), or post-bomb (1971-2008) values in the Ottawa tritium record . Potential mixtures of bomb peak and post bomb recharge fall within the transition zone.

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Figure 7

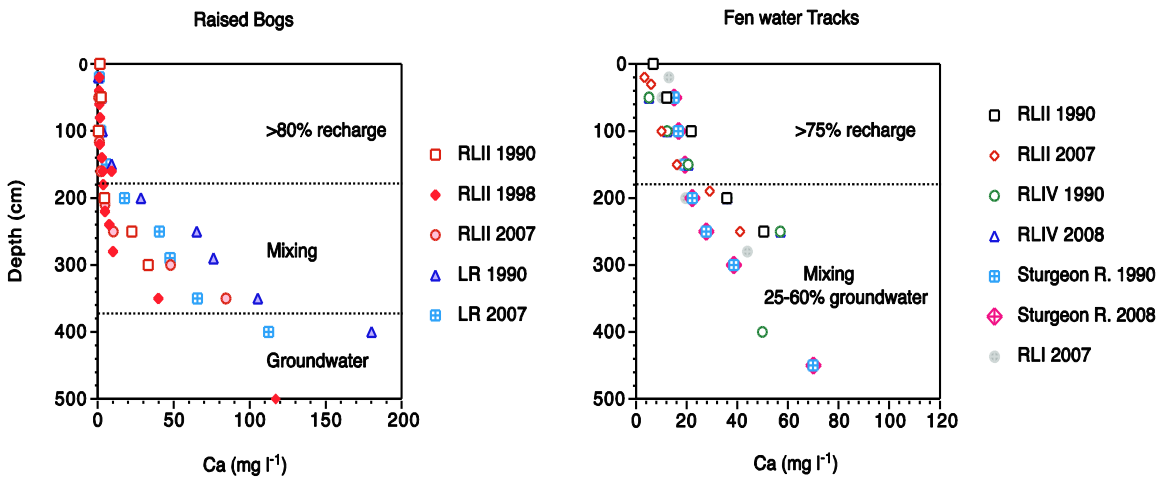

Figure 7. Ca profiles from a representative sample of bogs and fens across the GLAP from 1990-2007. The values for %recharge and %mixing with groundwater were calculated by binary mixing models. The sample sites are Red Lake II bog (RLII 1990, 1998, 2008), Lost River bog (LR 1990, 2007), Red Lake II fen (RLII 1990, 2007), Red Lake IV fen (RLIV 1990, 2008), and Sturgeon River fen (Sturgeon R. 1990, 2008). The locations for the sampling sites mentioned in the text are presented in Figure 1 or Romanowicz [1993]. Glaser et al. [1997], Chasar [2002], Dasgupta [2010], and Corbett [2012].

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Figure 8

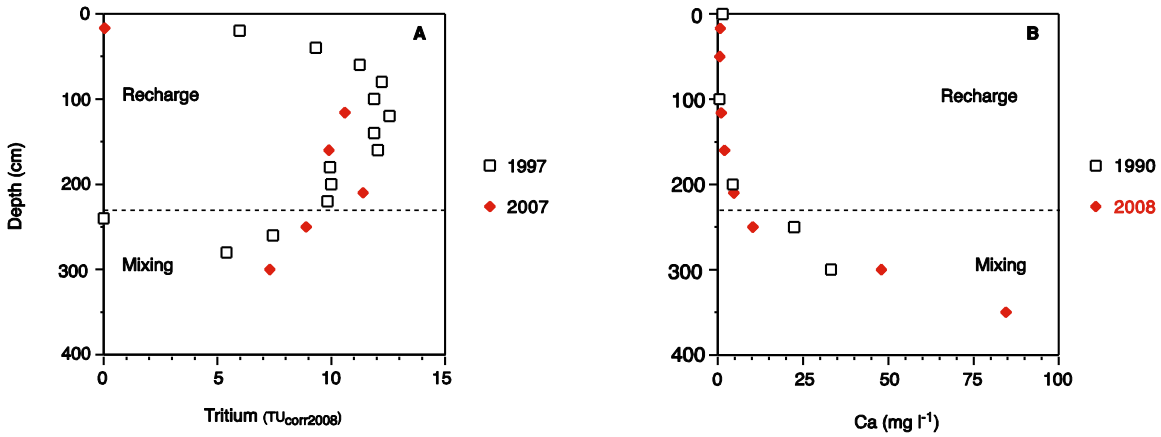

Figure 8. Comparison of tritium (A) and Ca (B) profiles from Red Lake II bog crest during 1997 and 2008. Zones for pore waters largely flushed by recharge or mixed with groundwater are marked. The decline in triitum corresponds to the rise in Ca indicating increasing mixing with groundwater below. Note change in depth scale from Figure 7.

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Figure 9

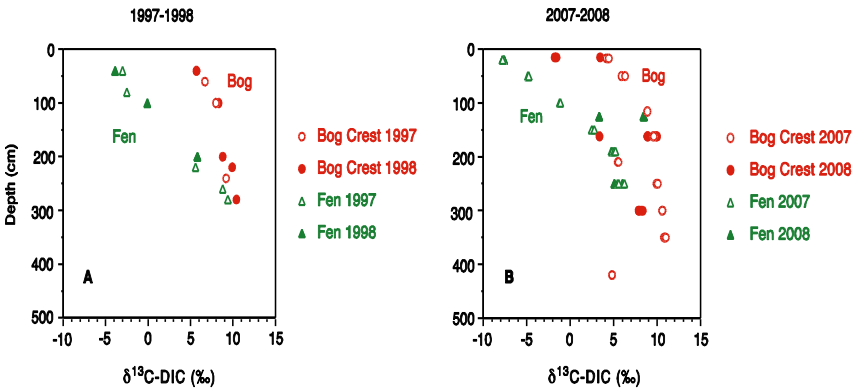

Figure 9. Comparison of $\delta^{13}C$ -DIC profiles in the Red Lake II bog-fen complex from 1997 though 2008. There was a substantial enrichment with respect to that of biomass (-27‰), atmospheric CO_2 (-8‰), and groundwater (-11‰).

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Figure 10

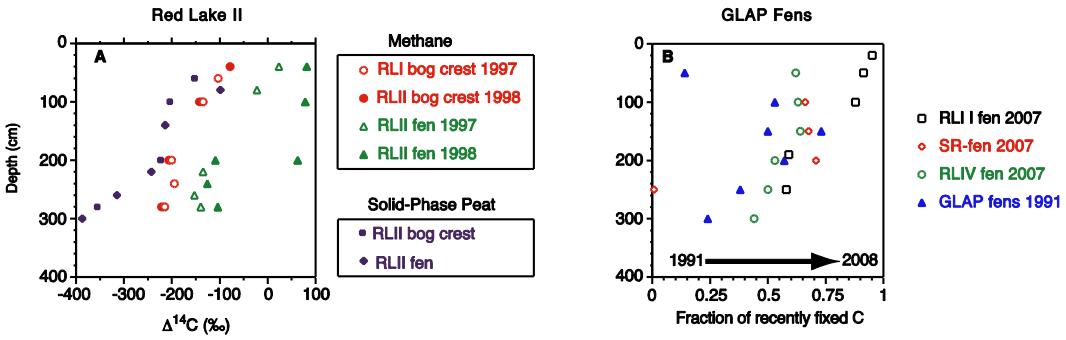

Figure 10. Enrichment of pore water methane in $\Delta^{14}C$ with respect to the solid-phase peat in the Red Lake II bog crest and fen site from 1997 to 1998 (A) and in fens across the GLAP from 1991 to 2008 (B).

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Figure 11

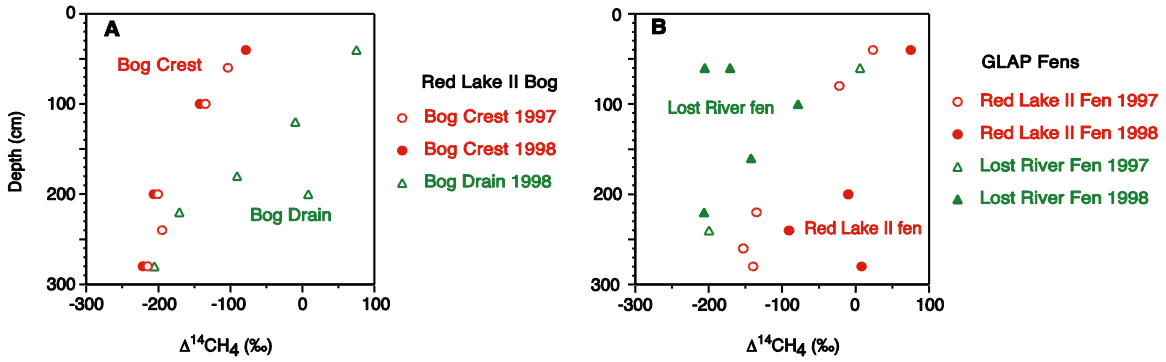

Figure 11. Methane is significantly enriched in $\Delta^{14}C$ within the pore waters of sedge-dominated sites (bog drain) relative to those from forested bog crests (A). In contrast, methane is significantly less enriched in $\Delta^{14}C$ within the sedge-dominated Lost River spring fen, which is located in a discharge zone for groundwater (B).

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Figure 12

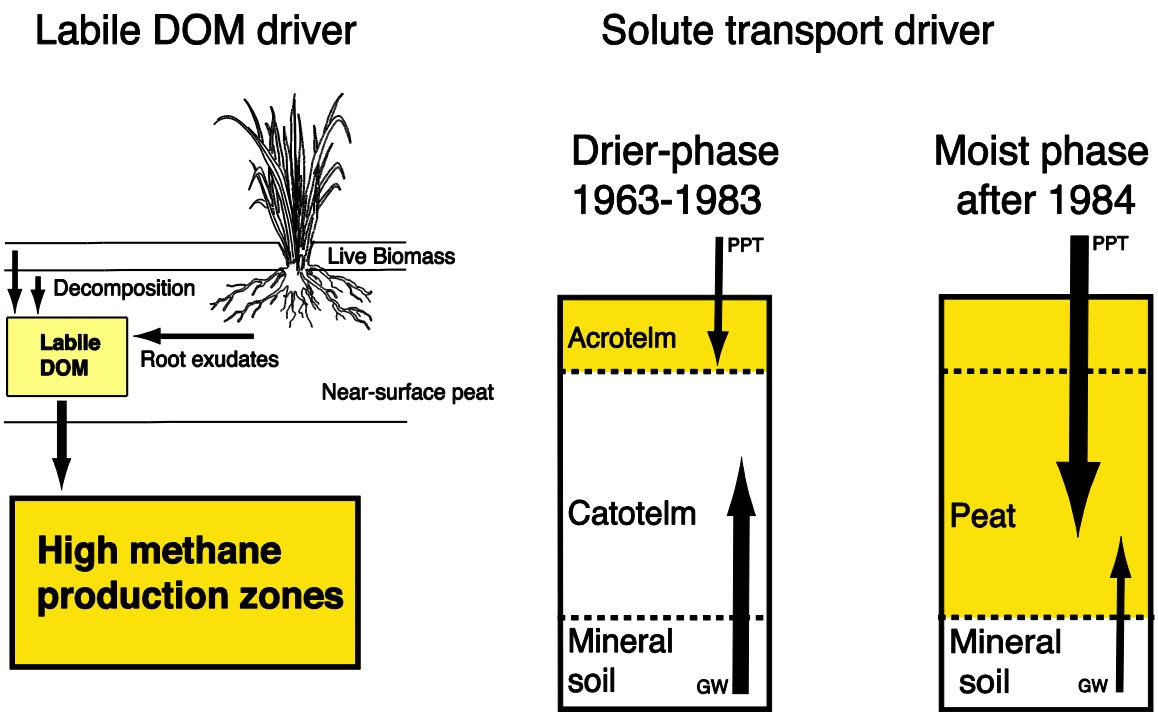

Figure 12. Linkage of climate to solute transport and methane production in the GLAP.

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